

EX-SITU ATOMIC FORCE MICROSCOPY STUDY OF THE INFLUENCE OF pH ON CALCIUM AND MAGNESIUM PRECIPITATION ON AN APATITE SURFACE¹

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Abstract

In this study, apatite crystal surfaces adjusted using potassium oleate to pH values of 8.0 and 5.0 were analyzed using atomic force microscopy (AFM). When the pH was adjusted to 8.0, the surface morphological analysis showed the presence of clusters on the apatite crystal surface formed by the reaction of potassium oleate with Ca^{2+} and Mg^{2+} ions, forming colloids of calcium dioleate ($\text{Ca}(\text{R-COO})_{2(s)}$) and magnesium dioleate ($\text{Mg}(\text{R-COO})_{2(s)}$). However, when the pH was adjusted to 5.0, it was not possible to identify the presence of clusters of $\text{Ca}(\text{R-COO})_{2(s)}$ and $\text{Mg}(\text{R-COO})_{2(s)}$ on the crystal surface. It is also thought that the precipitation of clusters and/or a set of clusters of calcium and magnesium dioleate on the apatite surface plays a key role in the ways collectors interact with the interfacial regions of the particles, impeding efficient separation by flotation.

Key words: Apatite; AFM; Micro-topography; Flotation.

ESTUDO EX-SITU DA INFLUÊNCIA DO pH NA PRECIPITAÇÃO DE CÁLCIO E MAGNÉSIO NA SUPERFÍCIE DA APATITA POR MICROSCOPIA DE FORÇA ATÔMICA

Resumo

Neste estudo apresenta-se uma análise da superfície de cristais da apatita, condicionados com oleato de potássio, para valores de pH igual a 8,0 e 5,0, por microscopia de força atômica (AFM). Quando o condicionamento foi realizado em pH igual a 8,0, a análise micromorfológica da superfície mostrou a presença de aglomerados na superfície dos cristais de apatita, formados pela reação do oleato de potássio com os íons Ca^{2+} e Mg^{2+} , formando o colóide dioleato de cálcio ($\text{Ca}(\text{R-COO})_{2(s)}$) e o dioleato de magnésio ($\text{Mg}(\text{R-COO})_{2(s)}$). Por outro lado, quando o condicionamento foi realizado em pH igual a 5,0, não foi possível identificar a presença dos aglomerados de $\text{Ca}(\text{R-COO})_{2(s)}$ e de $\text{Mg}(\text{R-COO})_{2(s)}$ na superfície dos mesmos. Acredita-se também que, a precipitação dos aglomerados e/ou conjunto de aglomerados de dioleato de cálcio e magnésio na superfície da apatita apresenta um papel determinante na natureza das interações entre os coletores e a região interfacial das partículas, interferindo na eficiência de separação por flotação.

Palavras-chave: Apatita; AFM; Microtopografia; Flotação.

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1 INTRODUCTION

The difficulty encountered in concentrating silicate-carbonate ore by flotation is closely linked to the chemical composition of the apatite, which varies significantly in different apatite-bearing rocks.^(1,2) Furthermore, the presence of significant concentrations of Ca^{2+} and Mg^{2+} plays a fundamental role in the adsorption of flotation reagents on the surfaces of semi-soluble minerals.^(3,4) The influence of these ions is increasingly considered one of the main factors affecting the selectivity of the floatation system.⁽⁵⁾

Adding a reagent system is not sufficient to attain the selectivity required by the floatation process. It is necessary to use mechanisms that act on the system, such as pH control, collectors tolerant to significant concentrations of calcium and magnesium ions, complexing agents and carbonate depressants.

The pH of the pulp plays an important role in ore floatation, since, to varying degrees of intensity, it affects the electrical charge on particle surfaces, dissociation of collector and depressant reagents in solution, adsorption of cations and anions on the mineral surface and the flocculation/aggregation state of particles present in the pulp. It is worth noting that, depending on the surface characteristics of the valuable and gangue minerals, there is a pH range within which adsorption of the collector reagent is selective in relation to gangue minerals.

The application of atomic force microscopy (AFM) has revealed new details on the adsorption of oleate and the precipitation of calcium ions on the mineral surface, as shown by the studies of Paiva et al.⁽⁶⁾ and Fa, Miller and Nguyen.⁽⁷⁾

Paiva et al.⁽⁶⁾ used AFM to investigate the effect of potassium oleate adsorption and calcium precipitation on the apatite surface. To do this, apatite crystals were adjusted *in-situ* using subsaturated solutions of calcium in the presence and absence of potassium oleate. In the images obtained by AFM and corresponding line profiles, the authors observed that the presence of calcium ions in the solution resulted in the formation of calcium carbonate/hydroxide precipitates and that oleate adsorption in the presence of calcium ions occurred in the form of clusters and/or a set of clusters of calcium dioleate. The presence of the clusters and/or set of clusters rendered the apatite surface heterogeneous and rough.

Fa, Miller and Nguyen⁽⁷⁾ used AFM to evaluate the interaction between calcium dioleate collector colloids and calcite and fluorite surfaces. The results obtained were analyzed in light of classic DLVO theory (*Derjaguin-Landau-Verwey-Overbeek*), determining the balance between the attractive and repulsive forces between the mineral particles and the calcium dioleate.

The authors observed that there was significant attraction between the calcium dioleate colloids and the fluorite surface, which could be attributed to hydrophobic attractive forces, without considering the oleate chemisorption process on the fluorite surface. On the other hand, measurements of the force of the direct interaction between the dioleate colloid and the calcite surface showed that the interaction was repulsive. The strong attraction observed therefore shows that the fluorite has a better response to floatation.

Studying the influence of pH on calcium and magnesium precipitation on the apatite surface is of fundamental importance for understanding the behavior of the apatite during the floatation concentration stage. In view of this affirmation, the aim of this study was to analyze the apatite surface by AFM after interaction between the particles (crystals) of apatite and the potassium oleate collector at pH values of 8.0

and 5.0. The concentrations of calcium and magnesium used in this study simulated the chemical conditions of the floatation pulp by the dissolution of carbonates.

2 MATERIAL AND METHODS

2.1 Sample

Natural apatite was used in this AFM study of the apatite surface. The natural apatite crystals were obtained from Ward's Natural Science Establishment (US) with the following composition: 16.7% P, 37.1% Ca, 0.6% Mg, 0.04% Al, 0.08% Si, 0.17% Na, 0.03% K, 0.5% Fe and 4.600 ppm F.

2.2 Reagents and Preparation of Solutions

The analytical grade reagents used, obtained from the VETEC Company, were oleic acid ($C_{18}H_{34}O_2$), potassium nitrate (KNO_3), calcium nitrate ($Ca(NO_3)_2$) and magnesium nitrate ($Mg(NO_3)_2$). All reagents were over 99% pure.

The solution of potassium oleate at a concentration of $4 \times 10^{-3} M$ was prepared in the presence of a KNO_3 electrolyte at a concentration of $10^{-4} M$. The solutions of $Ca(NO_3)_2$ and $Mg(NO_3)_2$ were prepared at a concentration of $2 \times 10^{-4} M$. All solutions were prepared using purified deionized water (Milli-Q, 18.2 M Ω . cm) and according to the methods adopted in each analysis.

2.3 Method

The analyses were conducted using the JPK Instruments Nanowizard® AFM at the COPPE/UFRJ laboratory, in intermittent contact mode, with NCR-10 (AIBS) or CSC11 (AIBS) probes manufactured by Nanoworld®.

The *ex situ* analysis initially involved obtaining images of the apatite particles which were washed in Milli-Q water using ultrasound, dried and then fixed to a glass plate. For the first analysis, the particles were adjusted in KNO_3 electrolyte ($10^{-4} M$) for 10 minutes before the AFM images were taken. After the first analysis, the same particles were adjusted to a pH of 8.0 or 5.0 using solutions of potassium oleate in the presence and absence of calcium and magnesium ions, stirred at 200 rpm for 40 minutes.

3 RESULTS

3.1 Results of the Micro-Topographic Analyses of Apatite Crystals Adjusted *Ex-Situ* to a Ph of 8.0

Figure 1 is a 2D micro-topographic image of the apatite crystal surface before adjustment using solutions of $Ca(NO_3)_2$ or $Mg(NO_3)_2$ in the presence of potassium oleate to a pH of 8.0 or 5.0. It shows a monotonous morphology with no superficial defects.

Figure 2 shows the 2D micro-topography of an apatite crystal adjusted using a solution containing potassium oleate and a significant concentration of Ca^{2+} ions. It reveals the presence of clusters and/or a set of clusters of varying diameter formed in the bulk by the interaction between the Ca^{2+} ions and the potassium oleate. Height

profiles 1, 2 and 3 (Figures 3, 4 and 5) show a set of clusters with diameters ranging from 2.0 μm to 3.5 μm .

When the crystal was adjusted using a solution containing potassium oleate and Mg^{2+} ions (Figure 6), the clusters and/or set of clusters are also present. In this case, the clusters and/or set of clusters are colloids of magnesium dioleate ($\text{Mg}(\text{R-COO})_{2(s)}$) formed in the bulk by the interaction between the Mg^{2+} ions and the potassium oleate. The diameters of these sets of clusters ranged from 1 μm to 1,5 μm (Figures 7, 8 and 9).

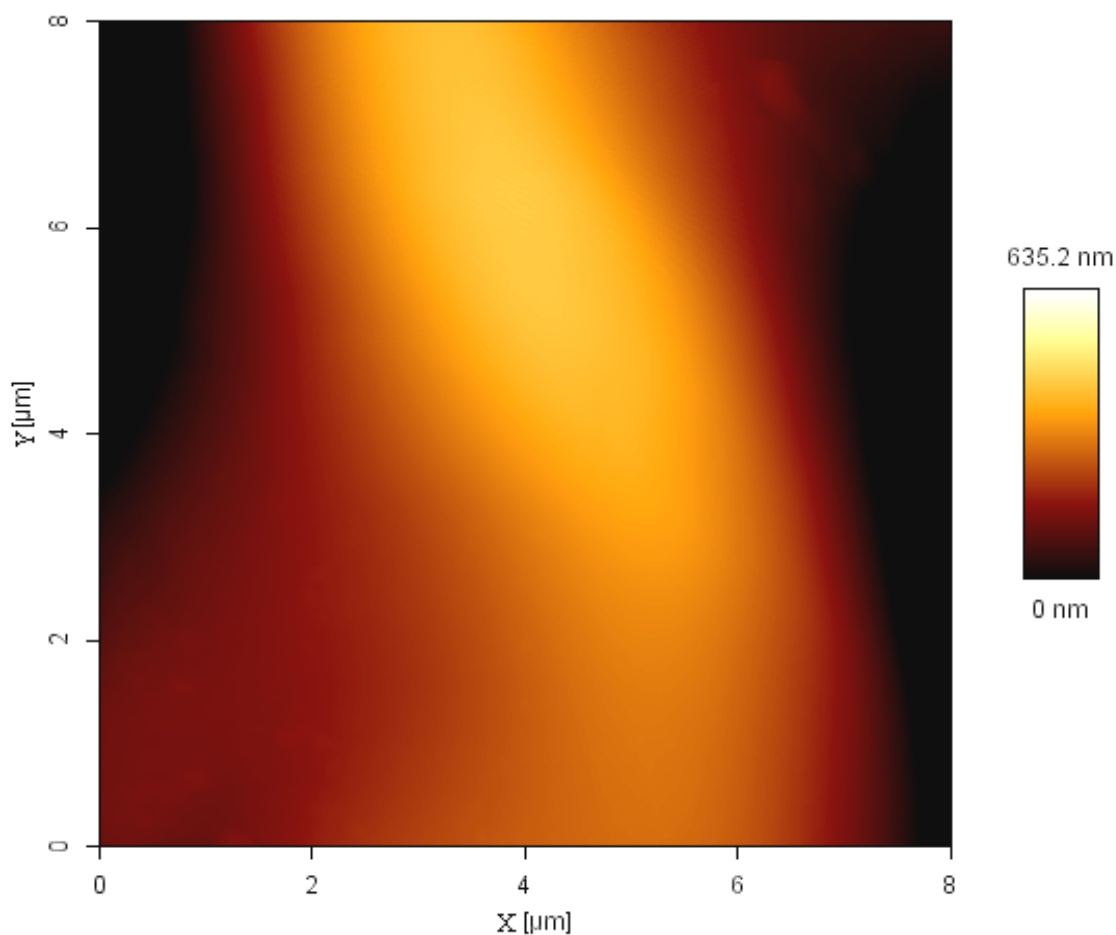


Figure 1. AFM 2D micro-topographic image of the crystal before *ex situ* adjustment using solutions containing significant concentrations of calcium or magnesium ions in the presence of potassium oleate.

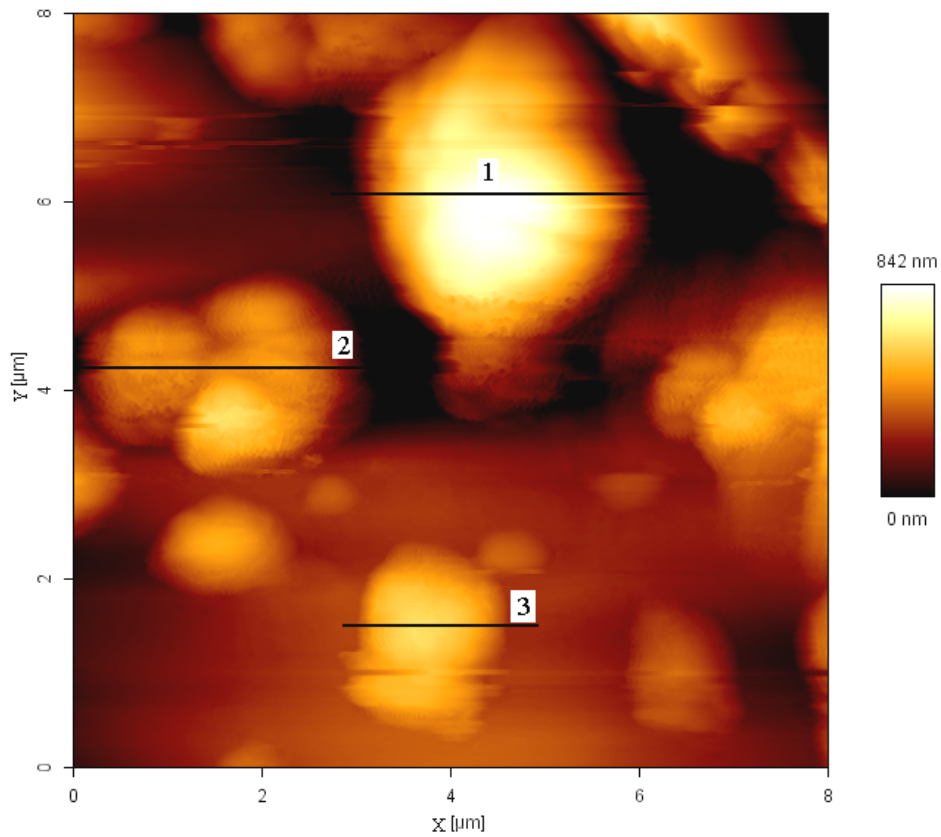


Figure 2. AFM 2D micro-topographic image of the crystal adjusted using a solution containing potassium oleate and calcium ions, showing the clusters and/or set of clusters of calcium dioleate precipitated on the surface of the apatite crystal.

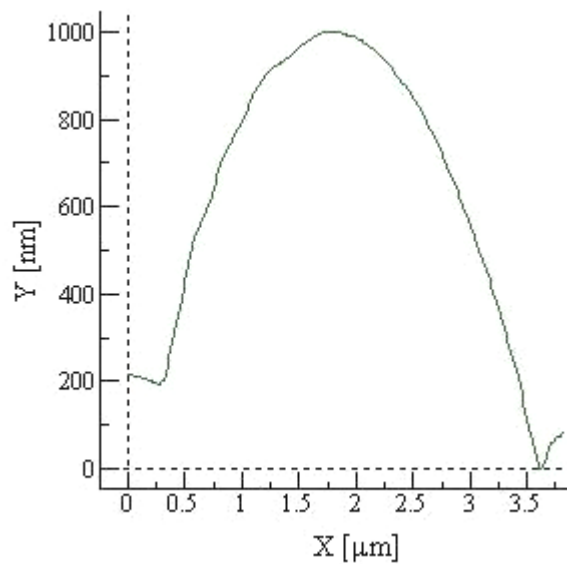


Figure 3. Height profile 1 showing the diameter of the cluster and/or set of clusters of calcium dioleate colloids precipitated on the surface of the apatite crystal.

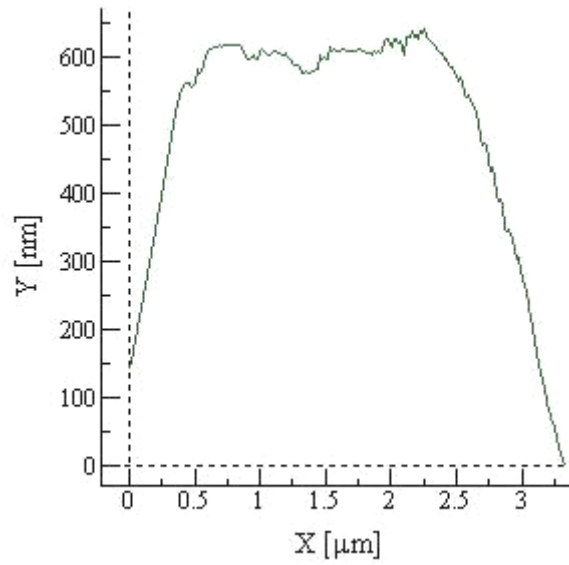


Figure 4. Height profile 2 showing the diameter of the cluster and/or set of clusters of calcium dioleate colloids precipitated on the surface of the apatite crystal.

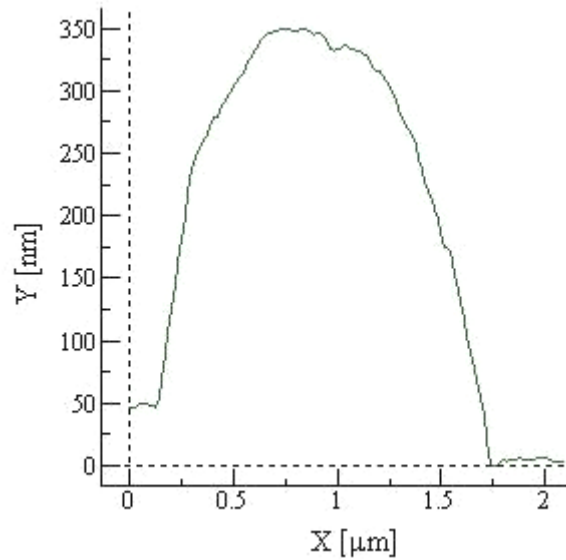


Figure 5. Height profile 3 showing the diameter of the cluster and/or set of clusters of calcium dioleate colloids precipitated on the surface of the apatite crystal.

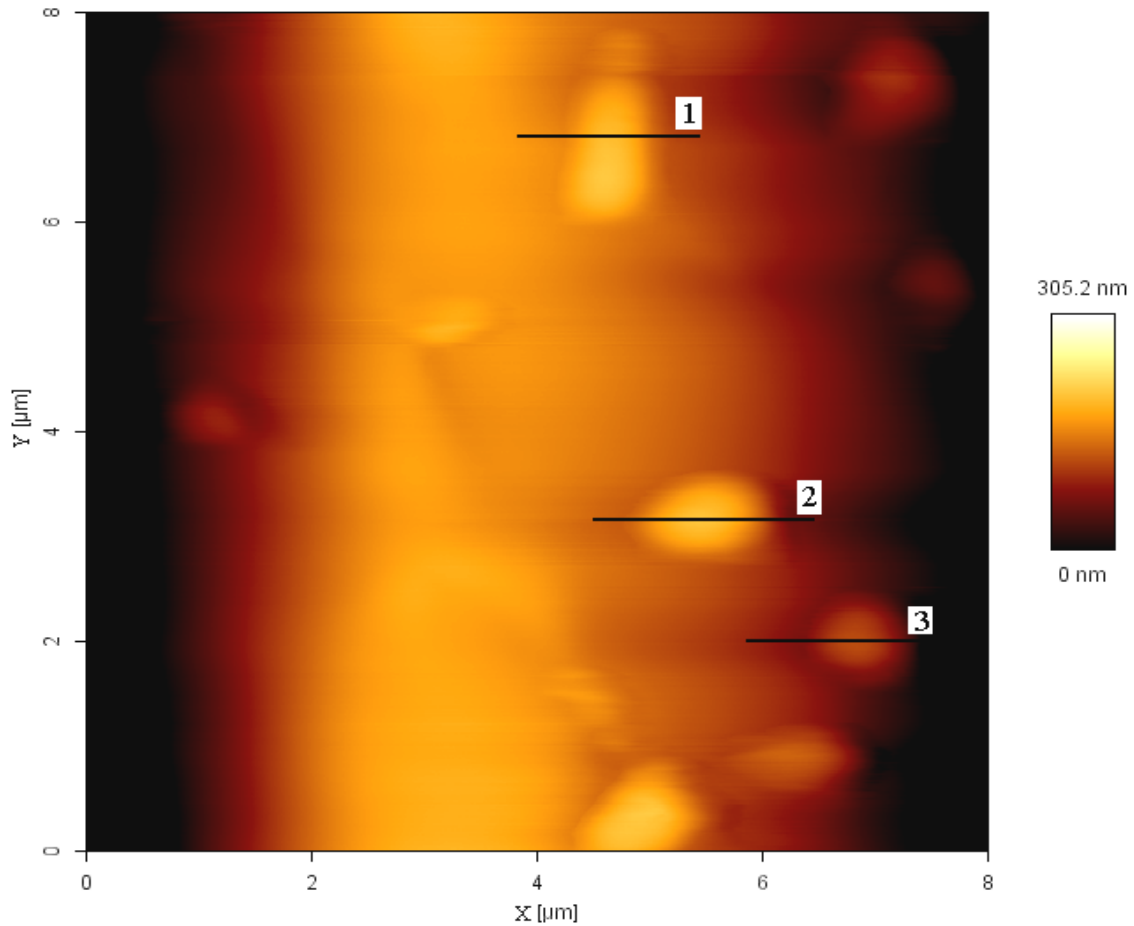


Figure 6. AFM 2D micro-topographic image of the crystal adjusted using a solution containing potassium oleate and magnesium ions, showing the clusters and/or set of clusters of magnesium dioleate colloids precipitated on the surface of the apatite crystal.

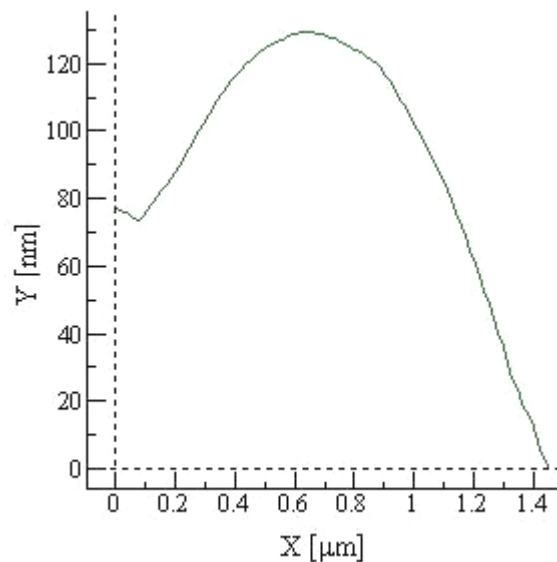


Figure 7. Height profile 1 showing the diameter of the cluster and/or set of clusters of magnesium dioleate colloids precipitated on the surface of the apatite crystal.

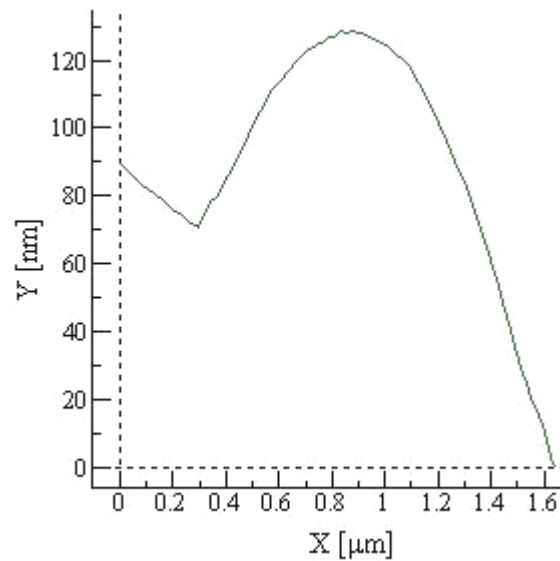


Figure 8. Height profile 2 showing the diameter of the cluster and/or set of clusters of magnesium dioleate colloids precipitated on the surface of the apatite crystal.

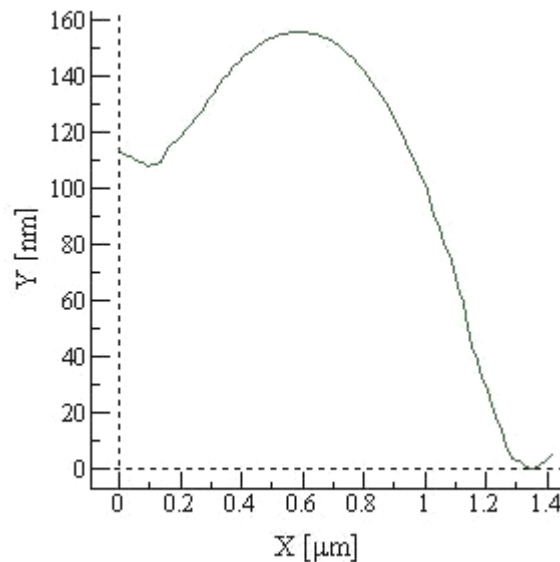


Figure 9. Height profile 3 showing the diameter of the cluster and/or set of clusters of magnesium dioleate colloids precipitated on the surface of the apatite crystal.

3.2 Results of the micro-topographic analyses of apatite crystals adjusted *ex-situ* to a pH of 5.0

Figures 10, 11 (calcium ions) and 12, 13 (magnesium ions) show that, after adjustment using $\text{Ca}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ in the presence of potassium oleate, there was no formation of clusters. It can also be seen that all the images obtained showed a clean surface, i.e. no inclusions and/or overlaps.

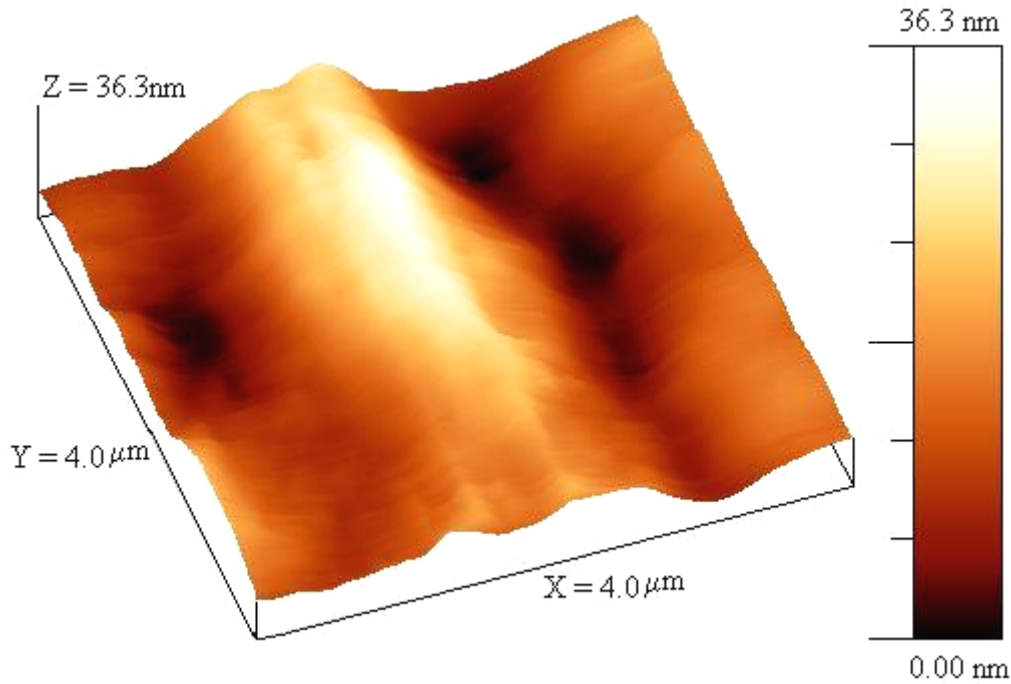


Figure 10. AFM 3D micro-topographic image of the crystal adjusted to a pH of 5.0 using a solution containing potassium oleate and calcium ions, showing a monotonous surface with no defects.

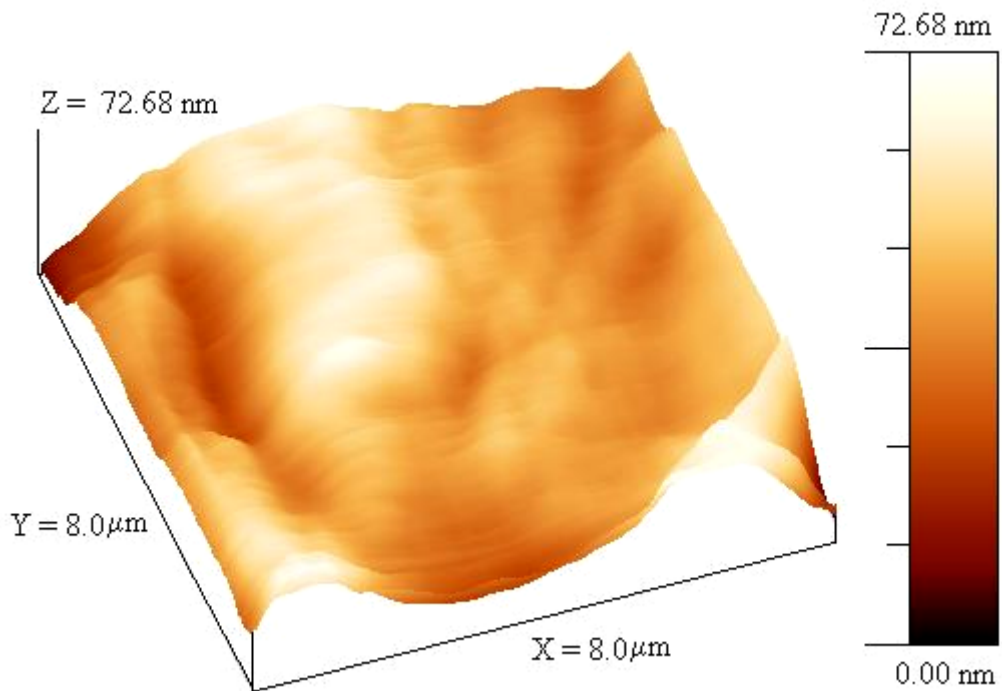


Figure 11. AFM 3D micro-topographic image of the crystal adjusted to a pH of 5.0 using a solution containing potassium oleate and calcium ions, showing a monotonous surface with no defects.

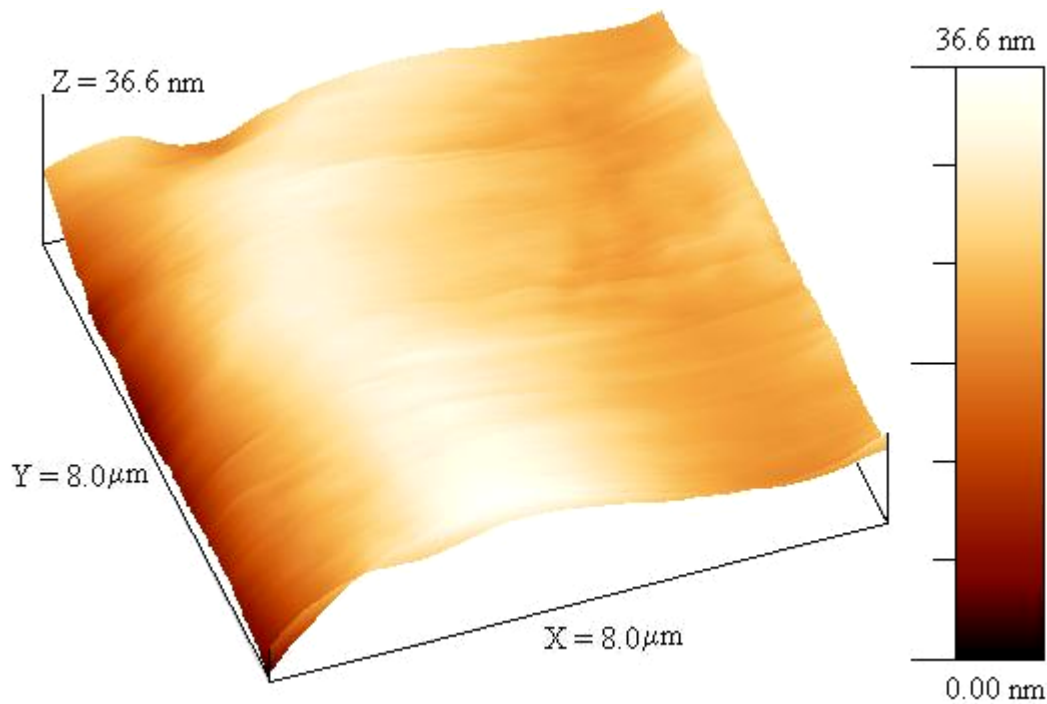


Figure 12. AFM 3D micro-topographic image of the crystal adjusted to a pH of 5.0 using a solution containing potassium oleate and magnesium ions, showing a monotonous surface with no defects.

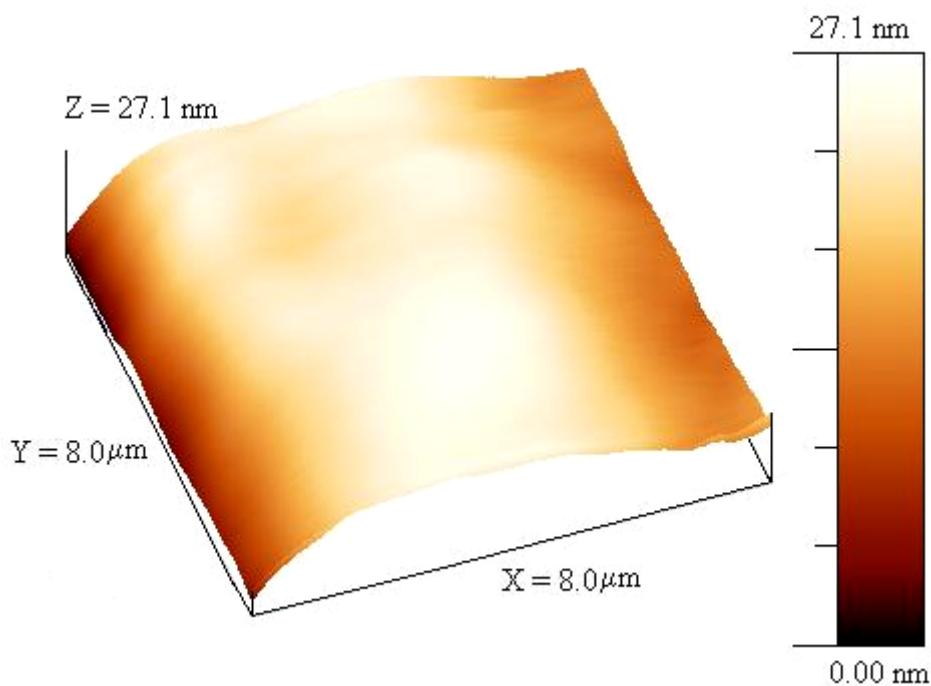


Figure 13. AFM 3D micro-topographic image of the crystal adjusted to a pH of 5.0 using a solution containing potassium oleate and magnesium ions, showing a monotonous surface with no defects.

4 DISCUSSION

Confirmation of the presence of clusters and/or sets of clusters of $Mg(R-COO)_{2(s)}$ and $Mg(R-COO)_{2(s)}$ on the surface of the apatite by micro-topographic analysis (Figures 2 and 6) of the crystals adjusted *ex-situ* backs up the hypothesis that this precipitation effect culminated in a significant modification of the physico-chemical properties of the apatite surface and these physical and/or chemical surface variations could be a

direct reflection of hydrophobicity, causing a drop in floatability. It is possible that there is a lower probability of surface adhesion to the air bubbles due to increased roughness.⁽⁸⁾

According to Finkelstein,⁽⁹⁾ precipitation of the calcium dioleate occurs when the following equation is true: $[Ca^{2+}] \times [R-COO^-]^2 > Kps > 10^{-15.6}$ mol/L (where: $[Ca^{2+}]$ = total calcium concentration in the solution; $[R-COO^-]$ = total oleate anions in the solution; and Kps = product of the solubility of calcium oleate, whose value is higher than $10^{-15.6}$ mol/L). Therefore, at the concentration of Ca^{2+} (2×10^{-4} mol/L) and oleate anions (4×10^{-3} mol/L) used, the Kps of the calcium oleate is 3×10^{-9} mol/L. Since the Kps value calculated for the concentrations of Ca^{2+} and $R-COO^-$ is higher than the Kps in the equation proposed, precipitation of the calcium oleate is confirmed. The same calculations can also be applied to the precipitation of magnesium dioleate.

These results corroborate the studies conducted by Paiva et al.,⁽⁶⁾ in which the authors confirmed that these clusters and/or sets of clusters are formed by the precipitation of calcium dioleate colloids. Furthermore, precipitation by saturation and the formation of an inorganic compound on the apatite surface have been studied by various authors.⁽¹⁰⁻¹⁵⁾

On the other hand, as can be seen in Figures 10, 11 and 12, 13, when the pH is adjusted to 5.0, formation of clusters and/or a set of clusters on the surface of the crystals does not occur. According to Somasundaran, Amankonah and Ananthapadmanabhan,⁽³⁾ dissolution or precipitation can be minimized by reducing the pH of the pulp. Thus, we can assume that if the apatite is in contact with a solution at a pH of around 5.0, precipitation on the apatite surface will not occur.

Figures 10 and 11 shows the formation of hills and valleys on the surface of the apatite crystal. This formation can be attributed to the dissolution reactions, the lines formed by the growth of the crystal itself and the shape and texture of the surface after breaking. The dissolution of the apatite occurs with the exit of fluorine, calcium and phosphorus ions^(16,17) forming voids (*etch-pits*). Furthermore, the dissolution of this sample led to the formation of stepped or rippled surface patterns on a nanometric scale, which become thicker after the 40-minute adjustment time used in this experiment.

5 CONCLUSIONS

The AFM images and corresponding line profiles showed the behavior involved in the interaction between the potassium oleate and the Ca and Mg^{2+} ions. Under the experimental conditions and by combining the oleate, Mg^{2+} and Ca^{2+} ions, calcium and magnesium dioleate were formed and precipitated in the form of clusters and/or a set of clusters on the surface of the apatite.

The presence of the clusters and/or a set of clusters can render the apatite surface heterogeneous and rough. The chemical heterogeneity that occurs on the surface and the roughness of the surface are decisive factors in floatability. The roughness is directly linked to particle adhesion to the air bubble in the floatation process. Therefore, particles with smooth surfaces have higher floatability than particles with rough surfaces.

It is also thought that the precipitation of clusters and/or a set of clusters of calcium and magnesium dioleate on the apatite surface plays a decisive role in the ways that collectors interact with interfacial regions of the particles, impeding efficient separation by floatation.

This study shows that AFM is a versatile tool for characterizing the behavior of the apatite surface, elucidating compositional and morphological characteristics (when dispersed in solutions containing significant concentrations of Ca²⁺ and Mg²⁺ ions) and consequently helping define and improve the processing route.

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