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Electrokinetic properties of wavellite and its floatability with cationic and anionic collectors

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ABSTRACT

The reverse apatite flotation with fatty acids has been widely used for the reduction of phosphorus content of magmatic origin iron ores. However, the occurrence of phosphorus intensely disseminated as secondary minerals such as wavellite renders the anionic reverse flotation a challenge. Zeta potential measurements and microflotation tests of wavellite with the use of anionic and cationic collectors were carried out in this work. The wavellite's IEP value was achieved at pH 4.5. Below the IEP value, the surface positively charged sites are made up of aluminum ions. The species H^+ , $Al(OH)_2^+$, $Al(OH)_2^{2+}$, Al^{3+} , OH^- , $H_2PO_4^-$, HPO_4^{2-} , and PO_4^{3+} , HPO_4^{2-} , HPO_4 play a role in the protonation and deprotonation reactions that will determine the wavellite-solution interface properties. The highest values of wavellite's floatability under basic pH conditions were achieved in the presence of cationic collectors (1×10^{-4} mol L⁻¹). The formation of surface complexes and the precipitation of insoluble salt of aluminum onto wavellite surface seems to be the most likely hypothesis for the chemical nature interactions between amines and wavellite. The surface formation of aluminum oleate on the wavellite's surface seems to be the most probable hypothesis for the adsorption mechanism and the resultant high floatability of wavellite between pH 7.5 and pH 10.0 in the presence of sodium oleate $(1 \times 10^{-4} \text{ mol } \text{L}^{-1})$. The results showed that the cationic reverse flotation of secondary phosphates is a promising route to reduce the phosphorus content of iron ores from deposits that underwent a supergene enrichment process, since wavellite floatability in the alkaline pH range, using amine as collector, was not significantly affected by the presence of corn starch.

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1. Introduction

Wavellite $[Al_3(PO_4)_2(OH)_3 \cdot 5H_2O]$ is a secondary aluminum phosphate that rarely forms crystals. When this occurs, its crystals have the form of radiated globular and spherulitic aggregates. It is crystallized in the orthorhombic-bipyramidal system and presents a perfect cleavage in the (1 1 0) plane and good cleavage in the (1 0 1) plane [1,2].

Wavellite is one of the most common secondary phosphate which occurs in the iron deposits with high phosphorus content. Phosphorus is an extremely harmful element in steel making, causing harmful effects in the product, such as increased hardness and brittleness and decreased ductility [3].

Phosphorus occurs in iron ores mainly as apatite. However, the occurrence of secondary phosphates, possibly recrystallized from primary phosphates, is very common in some iron deposits. While apatite occurs more frequently in Kiruna type magmatic hydro-thermal deposits [4–6], the secondary phosphates are more frequently found in deposits that underwent a supergene enrichment process. Phosphorus is also present in iron deposits adsorbed in the anionic form onto the surface of hydrated iron oxides, especially onto the goethite surface [7–11].

Minerals characterized as aluminum secondary phosphates are also common in igneous rocks and carbonatitic alkaline complexes. The presence of these phosphates generally does not interfere with the ore beneficiation process. However, the association of secondary phosphates with apatite particles through grains intergrowth or apatite surface coating decreases the flotation selectivity and consequently the total phosphorus recovery [12,13].

Phosphorus removal from iron ore concentrates has been a challenge for most iron ore operations, particularly in the case of origin other than magmatic. During the last decades most

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researchers have driven their studies to hydrometallurgical processes for phosphorus removal from iron ores of sedimentary and metamorphic deposits [14–18]. However the high cost and low efficiency of these processes prevented in many cases the industrial application. Despite the fact that a large amount of the phosphorus found in these types of deposits is intimately associated with the iron oxides surface or its crystal structure, there is now recognition that another significant portion of the element is associated with several secondary phosphate minerals [7,19,20]. In some cases the liberation may occur in a size range adequate for selective flotation between phosphates and iron minerals.

The reverse apatite flotation with fatty acids has been widely used for the reduction of phosphorus content of magmatic origin iron ores. This concentration process is usually preceded by magnetic separation and desliming stages [21–25]. However, the occurrence of phosphorus intensely disseminated as secondary minerals and adsorbed onto the iron hydroxides surface renders the anionic reverse flotation a challenge.

The shortage of fundamental studies addressing the physicochemical surface properties of wavellite and other secondary phosphates is one of the factors that hindered the development of selective flotation processes in the system under investigation. With the objective to bring some knowledge to the existing gap in the literature on such minerals, electrokinetic studies and microflotation tests of wavellite, with the use of anionic and cationic collectors, were carried out as a function of pH in this work. Another objective is to evaluate the results of wavellite microflotation and to search for potential application in flotation plant practice, opening the doors for the explotation and concentration of several iron ore deposits around the world which present phosphorus intensely disseminated as secondary minerals.

2. Experimental

2.1. Characterization and sample preparation

Tests were run on natural wavellite sample from Mauldin Mountain Ouarries, Mauldin Mt., Montgomery Co., Arkansas, USA. The wavellite sample was comminuted in a porcelain mortar and the coarser fraction $(-300 \,\mu\text{m} + 75 \,\mu\text{m})$ was used in the microflotation tests. The finer fraction $(-38 \,\mu\text{m})$ was utilized for the zeta potential measurements. The sample was submitted to a qualitative analysis using an X-ray diffratometer model PHILIPS PW 1710, Cu Kα radiation and a graphite monochromator crystal. The results were analyzed through the comparison of the values of the interplanar spacing and of the peaks intensities displayed in the diffractograms of the analyzed sample and a reference sample from the standard data base PDF-2 of the ICDD - International Centre for Diffraction Data. The software X'Pert HighScore version 2.1-2004 was also used. Amorphization domes were not observed in the diffratogram, indicating the absence of amorphous phases. The identified mineral phase was just wavellite, based on comparison with the standard number 74-2250 of the ICDD data base PDF-2.

2.2. Zeta potential measurements

The zeta potential measurements were carried out by the microelectrophoretic technique in the equipment Zeta-Meter System 3.0+ZM3-D-G with direct video imaging. The zeta potential values were calculated using the Smoluchowski equation.

Helium pycnometry analysis was performed using a Quantachrome NOVA 1200 and the wavellite sample's density achieved was 2.34 g cm⁻³. Samples of 0.025 g of the mineral in the size $-38 \mu m$ were added into 200 mL of the electrolyte solution in the preparation of the suspensions. The suspensions were settled during 24 h in such a way that the supernatant particles had a size below 5 µm, according with Stokes's Law. Sodium nitrate (NaNO₃) was used as supporting electrolyte at the concentrations 1×10^{-3} mol L⁻¹ and 1×10^{-5} mol L⁻¹. The pH values were adjusted with nitric acid (HNO₃) and sodium hydroxide (NaOH). The aluminum chloride hexahydrate (AlCl₃·6H₂O) was used at the concentration 5×10^{-3} mol L⁻¹ with the objective to evaluate the effect of aluminum ions on the wavellite surface characteristics, i. e., on the wavellite electrokinetic behavior. The tests were performed also in the presence of collectors (1×10^{-4} mol L⁻¹), and in these tests the pH values were adjusted with hydrochloric acid (HCl) and sodium hydroxide.

2.3. Microflotation tests

The microflotation tests were carried out in a modified Hallimond tube at selected pH values between 2 and 13. The air flow rate used was 30 mL min⁻¹. The volume of solution in the tube was 180 mL, and the wavellite weight was 1 g. The collector reagents used in the microflotation tests are presented in Table 1. The samples were conditioned with collectors during 5 min and the flotation time in all tests was 3 min. The reagents were prepared at the concentration 1×10^{-4} mol L⁻¹. The sodium oleate and octylamine used were of analytical grade, and Flotigam EDA is a commercial reagent manufactured by Clariant. The octylamine was 100% neutralized with acetic acid.

Some tests were also carried out in presence of corn starch, under alkaline pH, to check the potential depressant action of this reagent towards wavellite. The solubilization of corn starch was made by addition of sodium hydroxide at the weight ratio 5:1. The mineral was conditioned in a 90 mL volume of corn starch solution, at the concentration 10 mg L^{-1} , during 5 min. Immediately 90 mL solution of Flotigam EDA 20 mg L⁻¹ (resulting in 10 mg L^{-1} final concentration) was added. The collector conditioning time was 5 min and the flotation time was 3 min.

3. Results and discussion

3.1. Surface properties of wavellite

The aluminum in the wavellite crystal structure presents octahedral coordination with oxygen atoms, water molecules and hydroxyl groups. The aluminum octahedra are linked through hydroxyls in the opposing vertices forming two types of independent chains by sharp turns in alternating directions. The two different chains formed are linked by the PO_4^{3-} tetrahedra through the oxygen atoms of these groups. This type of arrangement creates dense layers of octahedra and tetrahedra in the plane (0 1 0) which are connected by alternated aluminum octahedra with water molecules. The strong chains of octahedra in the structure are clearly responsible for the fibrous habit of wavellite [26,27].

The principle of electrostatic valence elaborated by Pauling [28] indicates the exposition of aluminum ions (Al^{3+}) after the wavellite fragmentation. The electrostatic valence (electrostatic bonding strength) is equal to the charge or valence of the central cation of the polyhedron divided by its coordination number [29,30]. In the wavellite octahedra aluminum presents valence 3^+ and coordination number 6, resulting in an electrostatic force of $\frac{1}{2}$. Phosphorus in the tetrahedra presents valence 5^+ and coordination number 4. The electrostatic force will be equal to 1.25 a higher value than that of the aluminum octahedra. The bonding forces indicate, therefore, a greater stability of the phosphorus tetrahedra in comparison with the aluminum tetrahedra.

The chemical composition of wavellite and its crystalline structure suggest the rupture of the crystal in the planes containing

Table 1

Reagents used in the microflotation tests.

-		
Reagent	Chemical formula	Molecular weight $(g \text{ mol}^{-1})$
Flotigam EDA	$CH_3-(CH_2)_9-O-(CH_2)_3-NH_2$	215.37
Octylamine	$CH_3 - (CH_2)_6 - (CH_2) - NH_2$	129.24
Sodium oleate	$CH_3-(CH_2)_6-(CH_2)-CH-CH-(CH_2)-(CH_2)_5-(CH_2)-COONa$	304.44

water molecules. This rupture exposes a portion of the aluminum ions (Al^{3+}) and liberates them in solution in a non-stoichiometric form. Acid-base reactions (protonation and deprotonation) have been considered as determinant for the interfacial properties of apatite-solution. Considering this hypothesis, it can be estimated that these reactions would also impact the interface properties for the wavellite-solution systems.

3.2. Zeta potential measurements of wavellite

The results of wavellite zeta potential measurements in a wide pH range are presented in Fig. 1. The IEP value was achieved at pH 4.5, showing that above this pH value the negative surface sites in the Stern layer predominate.

Sparingly soluble minerals, like phosphates, may have its surface charge developed by non-stoichiometric dissolution that results in the hydrolysis of the ions released to the solution which in turn are capable of re-adsorption onto the minerals surface. The interactions between the ions of the crystal structure and the water hydrolysis products can also determine the phosphates surface charge. However, the definition of the generated surface species is still a challenge. The extremely complex structures, containing diverse substitutions, and their high solubility render impossible the determination of a constant for the solubility product of many phosphates. It is also enormously difficult the accurate determination of the surface species generated during the watermineral contact [31–36].

Vučinić et al. [37] evaluated the electrokinetic properties of hydroxiapatite and presumed that the surface ions Ca^{2+} , PO_4^{3-} , and OH^- participate in surface reactions similar to those reactions that occur in the bulk. They considered also that the hydroxiapatite surface charge would depend on the first order potential determining ions redistribution (Ca^{2+} , PO_4^{3-} , OH^-), while H^+ ions would be second order potential determining ions, regulating the concentration of ions or molecular species on the surface and in the solution.

Considering aluminum phosphates, the nature of potentialdetermining ions can be estimated based on electrokinetic behavior of the minerals and on distribution diagram of species for aluminum and phosphoric acid.



Fig. 1. Zeta potential curves for wavellite.

Huang and Keller [38] constructed a distribution diagram of species released during the dissolution of hydrated aluminum minerals in water. In accordance with the diagram, the species AI^{3+} , $AI(OH)_2^+$, and $AI(OH)^{2+}$ predominate until pH 4.5. The species $AI(OH)_2^+$ is the only predominant species between pH 4.5 and 7, while between pH 7.5 and 8.5 the species $AI(OH)_2^+$ and $AI(OH)_4^-$ predominate. The diagram presented by Huang and Keller [38] is very similar to the diagram obtained by Fuerstenau and Palmer [39] for 1×10^{-4} mol L⁻¹ for the species AI^{3+} .

The precipitation of species $Al(OH)_{3(s)}$ does not appear in the Huang and Keller [38] diagram, but it can be predicted to occur above pH 5.5 in the Fuerstenau and Palmer [39] diagram. Based on the data of these 2 diagrams and in the wavellite zeta potential curves obtained in the present work, one can foresee that the species Al^{3+} , $Al(OH)_2^+$, $Al(OH)^{2+}$, and $Al(OH)_4^-$ will participate in the protonation and deprotonation reactions that will determine the wavellite/solution interface properties.

The zeta potential increase (reduction of the negative values of zeta potential) along with the pH values reduction for wavellite (Fig. 1) indicates the chemical adsorption of hydrogen and aluminum ions developed from the wavellite dissolution at the negatively charged surface sites:

$$\equiv \mathbf{OH} + \mathbf{H}^+ \leftrightarrow \equiv \mathbf{OH}_2^+ \tag{1}$$

$$\equiv PO_4^{2-} + AI^{3+} \leftrightarrow \equiv PO_4AI^+ \tag{2}$$

$$\equiv HPO_4^- + Al^{3+} \leftrightarrow \equiv HPO_4Al^{2+}$$
(3)

$$\equiv HPO_4^- + Al(OH)_2^+ \leftrightarrow \equiv HPO_4Al(OH)_2 \tag{4}$$

$$\equiv HPO_4^- + Al(OH)^{2+} \leftrightarrow \equiv HPO_4Al(OH)^+$$
(5)

The species related to aluminum ions as well as the species related to the acids derived from phosphorus will be involved in the acidbase reactions. Considering the species distribution diagram for the phosphoric acid, the $H_2PO_4^-$ species predominates approximately between pH 2 and 7. The predominant species between pH 7 and 12 is the $HPO_4^{2^-}$ ion and the $PO_4^{3^-}$ ions predominate above pH 12 [36]. Thus, the increase of the negative value of the wavellite zeta potential above pH 4.5 indicates the adsorption of hydroxyl groups and the readsorption of anionic species developed from the wavellite dissolution in the active and positively charged surface sites:

$$\equiv \operatorname{Al}^{2+} + 2(\operatorname{OH}^{-}) \leftrightarrow \equiv \operatorname{Al}(\operatorname{OH})_2 \tag{6}$$

$$\equiv \operatorname{Al}^{2+} + 2(\operatorname{HPO}_4^{2-}) \leftrightarrow \equiv \operatorname{Al}(\operatorname{HPO}_4)_2^{2-} \tag{7}$$

$$\equiv \mathrm{Al}^{2+} + \mathrm{PO}_{4}^{3-} \leftrightarrow \equiv \mathrm{Al}\mathrm{PO}_{4}^{-} \tag{8}$$

The more negative values of zeta potential above pH 7 can be attributed to the adsorption of the species HPO_4^{2-} and PO_4^{3-} as shown in Eqs. (6)–(8).

To confirm the role of chemical constituents of wavellite as potential-determining ions, the effect of the aluminum species on the electrokinetic wavellite behavior was investigated. The IEP value was moved to pH 10 when aluminum chloride hexahydrate was used in the zeta potential measurements (Fig. 2), showing that aluminum ions play a significant role on the wavellite surface characteristics.

According to wavellite zeta potential data in the presence of sodium nitrate, it is assumed that neither nitrate nor sodium ion play a potential-determining ion role in the investigated system, since the IEP was not affected. However, the addition of aluminum ions rendered the mineral surface more positive above the isoelectric point, up to approximately pH 10. The change in zeta potentialdetermining or to the adsorption in the Stern Plane, as counterions. Interaction with other ions in the interfacial region by chemical and van der Waals bonds can be the reason to this adsorption, according to Eqs. (2)–(5).



Fig. 2. Zeta potential curve for wavellite in the presence of common ion.

3.3. Microflotation tests

The results of wavellite floatability and zeta potential determinations in the presence of sodium oleate are presented in Fig. 3. Sodium oleate changes the IEP from pH 4.5 to 3.5, where occurs the onset of hemimicelle formation. The continuous rise in the floatability extends to pH 7.5 and, between pH 7.5 and 10.0, the floatability was higher than 90%. Only the strong chemisorption of the collector is able to produce high floatability, since the collector and mineral surface are charged similarly, as indicated in the zeta potential curve.

According to the distribution diagram for acid oleic [40], the predominant species in the acidic region are neutral molecules (RCOOH), whereas species such as oleate ion (RCOO⁻), oleate dimer (RCOO)₂^{2–}, and the acid soap (RCOO)₂H⁻ exist in the basic region. In the pH range from 3.5 to 7.5, the increase in the negative zeta potential of wavellite indicates the chemisorption of oleate ions and neutral molecules, oriented by head groups toward the solid and by hydrocarbon chains toward the water solution, forming hemimicelles and rendering the surface hydrophobic (Fig. 4a). Van der Waals bonds between the hydrocarbon chains of the surfactant



Fig. 3. Floatability and zeta potential of wavellite with anionic collector. Reagent concentration: $1\times 10^{-4}\,M.$

immobilize the collector. The increase in the adsorption density of sodium oleate leads to maximal surface coverage in monolayer and between pH 7.5 and 10.0 the zeta potential values are unchanged, showing that the amount of chemisorbed species is independent of the pH in this region (Fig. 4b). Above pH 10.0 the wavellite floatability decreases abruptly from 90% to approximately 30% at pH 12.0. This decrease can be attributed to the adsorption of oleate dimers and oleate ions oriented by head toward the water (Fig. 4c), since the increase at the negative values of zeta potential above pH 10 can be observed until approximately pH 11.5.

The adsorption of fatty acids onto apatites in the alkaline pH range occurs essentially by means of chemical mechanisms. The interaction between the dissociated ions of these acids (anions) with the surface cations leads to the formation of insoluble salts at the surface of the mineral, as suggested by several authors [41–44]. This interaction can be represented by a specific reaction between the surface Ca cations and the RCOO⁻ anionic groups of the collector, forming calcium oleate at the surface:

$$\equiv CaOH + RCOO^{-} \leftrightarrow \equiv Ca^{+-}OOCR + OH^{-}$$
(9)

At the wavellite surface, the ions which react with the sodium oleate dissociated species are the Al cations. The formation of the insoluble salt aluminum oleate would be a reasonable hypothesis for the adsorption of sodium oleate and its derived compounds in the current floatability study. Moon and Fuerstenau [30] evidenced the formation of aluminum oleate at the spodumene (a lithium silicate) surface through the chemical interaction between the cationic aluminum surface sites and the carboxyl groups of sodium oleate, justifying the increased floatability of the mineral at pH 8. Several authors suggest the formation of calcium oleate at the apatite surface [37,41,43,45,46].

An analogous equation to the Eq. (9) could represent the adsorption of sodium oleate onto the wavellite surface in the alkaline pH region:

$$\equiv \operatorname{Al}(\operatorname{OH})_2 + 2\operatorname{RCOO}^- \leftrightarrow \equiv \operatorname{Al}(\operatorname{OOCR})_2 + 2\operatorname{OH}^-$$
(10)

The dissociated sodium oleate species would displace the hydroxyl groups from the surface sites leading to the formation of aluminum oleate at the surface. In fact, the formation of insoluble salts through the interaction between the carboxylic acid and cations like Fe²⁺, Ca²⁺, Cu²⁺, Mg²⁺, and Al³⁺ has been reported in the literature. Vijaya Kumar et al. [40] considered the following chemisorption reaction between the oleic acid and the sillimanite surface, at pH 7.5:

$$\equiv AIOH + RCOOH \leftrightarrow \equiv AIOOCR + H_2O \tag{11}$$

According to the authors, surface OH groups of sillimanite would lead to the deprotonation of the oleic acid with the formation of water molecules. The displacement of OH groups from the surface sites would expose the Al cations and promote the adsorption of the deprotonated acid with the formation of an insoluble aluminum salt. The same authors evaluated the addition of oleic acid to solutions containing Al³⁺. The formation of aluminum oleate precipitate was not detected, indicating that the interaction only takes place with the metal hydroxide.

The formation of aluminum hydroxy complexes must also be considered. The wavellite solubility would lead to the nonstoichiometric dissolution of Al surface ions that would form aluminum hydroxides in solution which subsequently would readsorb at the mineral surface (negatively charged) through hydrogen bonds. These ions in the surface can favor the adsorption of the collecting reagents.

Fig. 5 illustrates the results of wavellite floatability with Flotigam EDA and octylamine. The adsorption of amine onto wavellite can be attributed to both chemical and electrostatic interactions.



Fig. 4. Proposed scheme for interaction mechanisms between sodium oleate and wavellite surface, at different pH ranges.

Octylamine addition shifts the IEP of wavellite from pH 4.5 to 7.0 and Flotigam EDA changes the IEP to pH 8.5. In the presence of octylamine, the onset of hemimicelle formation occurs at pH 7.0, where the surface becomes negative. However, in the presence of Flotigam EDA, the onset of hemimicelle formation occurs before the IEP, where the surface is still positively charged.

The dissociation of amine can be described by the equilibrium:

$$RNH_{2(aq)} + H_2O \leftrightarrow RNH_3^+ + OH^-$$
(12)

In acidic and neutral pH range amines are completely dissociated. As solution is made progressively alkaline, the formation of undissociated species ($RNH_{2(aq)}$) increases. At pH 10.6 the extension of dissociation is approximately 50% [47].



Fig. 5. Wavellite floatability and zeta potential with cationic collectors. Reagents concentration: $1\times 10^{-4}\,M.$

The adsorption of octylamine and Flotigam EDA onto wavellite surface can be result of hydrogen bonds between neutral surface sites and amine dissociated species, similarly as proposed by Chernyshova et al. [48] for interaction between amine and quartz:

$$\equiv \text{AIOH} + \text{RNH}_3^+ \leftrightarrow \equiv \text{AIOH}_{2...}^+ \text{NH}_2 \text{R}$$
(13)

As result of this adsorption, the IEP values becomes higher, i.e., the surface becomes more positively charged as can be seen in Fig. 5.

Amines can also undergo additional intramolecular reactions in aqueous media, forming ionomolecular complexes $(RNH_2RNH_3)^+$ by association of aminium ion and neutral amine molecule and dimerization of aminium ions $(RNH_3)_2^{2+}$ [47]. These species are highly surface active and certainly participate of the reactions of adsorption onto wavellite:

$$\equiv \operatorname{AlOH} + (\operatorname{RNH}_2\operatorname{RNH}_3)^+ \leftrightarrow \equiv \operatorname{AlOH}_{2...}^+ (\operatorname{NH}_2\operatorname{R})_2 \tag{14}$$

$$\equiv \operatorname{AlOH} + (\operatorname{RNH}_3)_2^{2+} \leftrightarrow \equiv \operatorname{AlOH}_{2...}^+ (\operatorname{NH}_2 R)^+ (\operatorname{NH}_3 R)$$
(15)

Until approximately pH 10.6, the reactions (13)–(15) can describe the adsorption of amine onto wavellite and justify the high floatability values, near to 100%. Above this pH value, the continuation of the maximum floatability values could be explained by the adsorption of molecular species (RNH_{2(aq)}) jointly with the adsorption of dissociated species. Since the concentration of dissociated species above pH 10.6 is low, it is possible that wavellite requires small amounts of surface active collecting species to become hydrophobic. A general scheme proposed for interactions between amines and wavellite is presented in Fig. 6.

Adsorption of amine onto wavellite may also be considered as result of precipitation of insoluble salt of aluminum onto wavellite surface. This adsorption would be result of ion-exchange reactions between the mineral anion and the collector cation. The formation of surface complexes seems also to be a hypothesis for the chemical nature interactions.

Flotigam EDA yielded higher values of floatability than octylamine until pH 9.8. These results can be explained by the chemical characteristics of the reagents. Flotigam EDA presents the polar group $O-(CH_2)_3$ between the radical R and the polar head NH₂ of the primary amine. This characteristic strengthens the collector adsorption due to a possible hydrogen bond $O-H\cdots O$ between the surface hydroxyl group of the mineral and oxygen in the collector structure [49]. According to Araujo et al. [50], the presence of the extra hydrophilic group promotes collector adsorption at liquid–gas interfaces and enhances the elasticity of the liquid film around the bubbles.

Fig. 7 illustrates the results of wavellite floatability in the presence of Flotigam EDA and starch. The maximum floatability values were achieved between pH 9.7 and 10.7. The steep drop







○ Flotigam EDA ★ Flotigam EDA and corn starch

Fig. 7. Wavellite floatability with amine in the presence and absence of corn starch. Reagents concentration: 10 mg L^{-1} .

in floatability beyond pH 7 may be explained by the use of low collector concentration, namely $5 \times 10^{-5} \text{ mol L}^{-1}$. Even at this concentration the effectiveness of the starch depressing action may be evaluated.

The wavellite floatability was not significantly affected by the presence of corn starch. The explanation for these results may be based in complexes formation between corn starch and active sites at the wavellite surface.

The adsorption of corn starch onto calcite has been explained by formation of complexes between the starch hydroxyl groups and Ca cations, like Ca²⁺ and CaOH⁺, at the mineral surface. The decrease in starch adsorption coincides with the drop in the concentration of these cations with the increase in pH [33,34]. In the case of wavellite, the drop in Al cations (Al³⁺, Al(OH)⁺₂, Al(OH)²⁺) concentrations should inhibit the formation of complexes between starch and wavellite surface active sites, preventing adsorption. Sterical hindrance effects may also be considered, for the position of hydroxyl groups in starch may not fit the spacing between wavellite surface active sites.

4. Conclusions

The wavellite chemical composition and crystalline structure suggest the rupture of the crystal in the planes containing water molecules. This rupture exposes a portion of the aluminum ions (Al³⁺) and liberate them in solution in a non-stoichiometric way. The IEP of wavellite was achieved in the pH value 4.5 and the effect of the aluminum species on the electrokinetic wavellite behavior was confirmed. The species H⁺, OH⁻, Al³⁺, Al(OH)₂⁺, Al(OH)²⁺, H₂PO₄⁻, HPO₄²⁻, and PO₄³⁻ will take part in the protonation and

deprotonation reactions that will determine the wavellite-solution interface properties.

Wavellite presented high floatability with sodium oleate at the concentration 1×10^{-4} mol L⁻¹ between pH 7.5 and 10. The surface formation of aluminum oleate through the interaction between sodium oleate and wavellite is the most probable hypothesis for the adsorption mechanism and the resultant high floatability of wavellite in this pH region. Above pH 10.0 the wavellite floatability decreases abruptly from 90% to approximately 30% at pH 12.0.

Wavellite presented around 100% of floatability up to pH 8.2 with Flotigam EDA and up to pH 9.8 with octylamine, both at the concentration 1×10^{-4} mol L⁻¹. The zeta potential results indicated that adsorption of amine onto wavellite can be attributed to both chemical and electrostatic interactions, since octylamine addition shifts the IEP of wavellite from pH 4.5 to 7.0 and Flotigam EDA changes the IEP to pH 8.5. Flotigam EDA yielded higher values of floatability than octylamine until pH 9.8 and these results can be explained by the presence of the polar group O–(CH₂)₃ in the Flotigam EDA structure, increasing its collecting power and enhancing the elasticity of the liquid film around the bubbles.

The results of wavellite floatability with Flotigam EDA in the presence of corn starch showed that the cationic reverse flotation of secondary phosphates can open the doors for the explotation and concentration by selective flotation of several iron ore deposits around the world which present phosphorus intensely disseminated as secondary minerals, since wavellite floatability in the alkaline pH range, using amine as collector, was not affected significantly by the presence of corn starch.

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