Floatability of Fe-bearing silicates in the presence of starch: Adsorption and spectroscopic studies

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Abstract. Natural polysaccarides such as starch, dextrin, cellulose and their derivatives are promising non-toxic and biodegradable organic flocculants and flotation depressants. This paper presents the investigation of mechanism of adsorption of corn starch on quartz and Fe-bearing amphibole, i.e. pargasite. The direct measurement of starch adsorption on the mineral surfaces shows no difference between quartz and pargasite. However, the starch adsorption on the magnetite is more important. FT-IR spectroscopy studies reports different adsorption mechanism of starch on quartz and pargasite surface. The key changes observed in starch absorption on quartz are the major shifts in C=O stretching frequencies presumed existence of a hydrogen bond between starch and quartz surface. The similar changes were observed in this region of IR-band for pargasite. The appearance and disappearance of the bands in the region 960-920 cm⁻¹ corresponds probably to formation of a new chemical bond between starch O-H groups and metal atoms on pargasite surface with formation of a surface complex. This result confirms that adsorption of the starch on the pargasite surface is droved by two mechanism. Hence, existence of strong chemical bond between starch and pargasite surface explains decrease of its floatability compared to quartz in process of iron ore flotation and forces to search new conditioning reagent modes.

1. Introduction

Selective flocculants and depressants are indispensable in any flotation reagent scheme targeting selective separation of different minerals. Natural non-toxic and biodegradable polysaccharides such as starch, dextrin, cellulose and their derivatives are widely applied as selective flocculants and depressants in froth flotation. All of these applications involve adsorption of the polysaccharides onto minerals.

Corn starch is the most used flocculant and depressant in reverse cationic flotation of iron ores due to its selectivity and availability in large amounts. As confirmed by investigations [1,2], starch adsorption is selective for quartz and iron oxides. Adsorption layer of starch on quartz is some times less dense that on hematite. N S Mikhailova [2,3] determined that starch adsorption on quartz and hematite is different not just by magnitude, but also by attachment strength. At pH 8 to 11, washing of inactivated quartz allows to remove 80% of adsorbed starch while starch retains intact on hematite surface while washing it. High attachment strength of starch on hematite proves specific interaction...
between starch and iron oxide surface take place. It is also confirmed by fact that amylopectin (starch consists two components – amylose and amylopectin) reacts so strongly with iron (III) in solution [4]. Therefore, the specific affinity of iron minerals for starch can complicate the flotation separation between iron oxides and Fe-bearing silicates as micas and amphiboles, which are presented in the Banded Iron Formations (BIF). In this paper, we report on the adsorption of starch onto magnetite, quartz and Fe-bearing amphibole, i.e. pargasite.

Several mechanisms for the adsorption of starch and related polysaccharides onto minerals have been proposed. In the early studies, hydrogen bonding was proposed as the primary adsorption mechanism of polysaccharides on mineral surfaces [1]. Hydrophobic bonding was suggested by Wie and Fuerstenau [5]. Adsorption by means of electrostatic interaction of starch with quartz and hematite surface is also discussed [1]. Later, chemical interaction was proposed as significant adsorption mechanism [4,6-8]. The aim of this study was to investigate the interaction between corn starch and pargasite, and to make a comparison with the adsorption mechanism onto quartz. This involved diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) and adsorption experiments.

2. Experimental

2.1. Materials

Commercial quartz was purchased from Merck, and a sample of natural magnetite was supplied from Lebedinsky deposit, Kursk region, Russia. Pargasite sample is a natural mineral, however, its origin is not known. Quartz and pargasite samples were prepared by dry ground. The ground pargasite sample was repeatedly passed through a magnetic separator to obtain clean pargasite mineral to be used in the experiments. The ground samples of quartz and pargasite were then dry screened through 53 μm BSS sieve. The -53+10 μm size fractions were used for adsorption tests whereas -10 μm fractions, received by sedimentation, were used for DRIFT measurements. Magnetite sample was already ground and represented a magnetic concentrate of -53+10 μm size fraction. The specific surface areas, chemicals and mineralogical compositions of -53+10 μm size fraction of the samples were determined by BET method with nitrogen as the adsorbate, as well as by ICP-AES and XRD methods. All these methods are summarised in table 1.

| Property                | Magnetite | Quartz | Pargasite |
|-------------------------|-----------|--------|-----------|
| Specific surface area (m²/g) | 0.8       | 1.0    | 1.1       |
| Chemical analysis (%)    |           |        |           |
| Fe₂O₃                   | 66.9      | 13.3   |           |
| FeO                     | 29.3      |        |           |
| SiO₂                    | 2.8       | 100    | 40.5      |
| Al₂O₃                   | 0.1       | 14.1   |           |
| MgO                     | 0.2       | 13.0   |           |
| TiO₂                    |           | 1.7    |           |
| CaO                     | 0.1       |        | 11.0      |
| Na₂O                    |           |        | 1.9       |
| Mineral composition     | Magnetite, hematite, amphiboles, quartz | Quartz | Pargasite, chlorite |

Starch used in studies is corn starch, purchased from Sigma. Its amylopectin and amylose contents are 73% and 27%, respectively. Starch is dissolved by alkali gelatinisation with adding NaOH and stored in 0.1 g/L concentration. The starch solution was freshly prepared daily to avoid the degradation. Reagent grade NaOH is used for pH adjustment. Milli-Q water is used in all experiments.
2.2. Methods

2.2.1 Adsorption tests. In these experiments, 0.5 g of mineral particles is placed in 50-mL adsorption bottles with an aqueous solutions of starch of various concentration, at pH 10. After a 12 hours of conditioning on digital horizontal shaker at room temperature, the particles were separated and liquid was centrifuged at 12000 G in order to obtain the supernatants required for the starch analysis. The starch residual concentrations in the obtained supernatants were determined by total organic carbon (TOC) analysis using the TOC-V CSH Shimadzu analyzer. The TOC value is the difference between measured total carbon (TC) and inorganic carbon (IC). The starch adsorbed was determined from the difference between the initial and residual starch concentrations.

2.2.2 DRIFT spectroscopy. The FTIR spectra are obtained with a Bruker Equinox 55 spectrometer with its own diffuse reflectance attachment. Typical spectrum was an average of 200 scans measured at 4 cm\(^{-1}\) resolution. The following experiment was carried out, and corresponding infrared spectra were recorded: 0.2 g of mineral powder is placed in contact with an aqueous solution of starch, with a concentration of 0.1 g/L, at pH 10. After a 60-min agitation using a digital horizontal shaker at room temperature, the particles were separated by filtration using filter paper and dried at room temperature on air. KBr pellets were prepared, containing suitable amounts of mineral particles, which are expected to carry adsorbed species on their surfaces.

3. Results and discussion

3.1. Adsorption studies

Adsorption density of starch on magnetite, quartz and pargasite as a function of its initial concentration in the solution at pH 10 is shown in figure 1. It can be observed that adsorption density on magnetite is higher than on quartz and pargasite, both of them adsorb close amounts of starch. Maximum adsorption on magnetite reaches 6.38 mg/m\(^2\) and it is 4.54 mg/m\(^2\) on quartz. At concentrations below 200 mg/L, starch adsorption on magnetite and quartz is linear as indicated by the data. This confirms theory [9] that free starch molecules adsorb at active sites of mineral surface until saturation is reached.

![Figure 1](starch吸附图.png)

*Figure 1. Starch adsorption density of magnetite, quartz and pargasite as a function of starch concentration, pH 10.*
3.2. Infrared diffuse reflectance spectral studies

Analysis of IR-spectra before and after the starch treatment indicates that major changes during the treatment are found in the high-frequency area. Intensity increase and shift of the wide band centred at 3385 to 3379 cm\(^{-1}\) (6 cm\(^{-1}\)) which corresponds to O-H stretch as well appearance of the band at 2929 cm\(^{-1}\) corresponding to C-H stretching \[10\] confirm starch adsorption on quartz (figure 2). The position decrease of O-H stretching band can suggest an increase in the number of hydrogen bonds. However, it is difficult to prove that hydrogen bonds are formed between starch hydroxyl groups and quartz hydroxyl groups because intermolecular hydrogen bonds (band at 3350 cm\(^{-1}\)) are already present in starch molecules. Nevertheless, the presence or absence of hydrogen bonds between starch and mineral surface can be estimated by infrared bands in the region 1080-1000 cm\(^{-1}\) associated with the C-O stretch coupled to the C-C stretch and O-H deformation of starch molecules.

Hence, the band shift from 1042 to 1033 cm\(^{-1}\) and a certain band deformation presumes existence of a hydrogen bond between starch and quartz surface. No other changes of IR-bands were observed, although a weak band at 800 cm\(^{-1}\) can be detected corresponding to O-H bending in silanol groups \[11,12\].

![Figure 2. DRIFT spectra of (a) quartz and (b) starch adsorbed on quartz.](image)

Starch adsorption on pargasite is confirmed by the reduction of O-H stretching frequency from 3552 to 3546 cm\(^{-1}\) (6 cm\(^{-1}\)) and from 3408 to 3394 cm\(^{-1}\) (14 cm\(^{-1}\)), increase of O-H deformation frequency for water molecules from 1637 to 1647 cm\(^{-1}\) (10 cm\(^{-1}\)) as well as appearance of adsorption bands for C-H stretching at 2932 cm\(^{-1}\), O-H in-plane deformation at 1419 cm\(^{-1}\) coupled with C-H deformation at 1329 cm\(^{-1}\) (figure 3). The appearance of the band at 953 cm\(^{-1}\) and its disappearance at 924 cm\(^{-1}\), correspond probably to formation of a new chemical bond between starch hydroxyl groups and metal atoms (Fe, Al, Ca) on pargasite surface with formation of a surface complex \[4,6,7\].

Certain band shift from 1012 to 1005 cm\(^{-1}\), corresponding to C-O stretch coupled with C-C stretch and O-H deformation, may point to the presence of a hydrogen bonds between starch hydroxyl groups and surface hydroxyl groups, such as silanols, unable to participate in surface complexation.
4. Conclusions
Adsorption and infrared spectroscopy studies have shown that starch is adsorbed both on quartz and pargasite. The main band shift in the region of 1080-1000 cm\(^{-1}\) for quartz shows that starch attaches to the surface by means of hydrogen bonds between starch hydroxyl groups and surface silanols of quartz. In case of pargasite, two starch absorption mechanisms are possible: by means of hydrogen bonds with the surface silanols of amphibole as well as by means of formation of chemical complex with metal atoms on the surface.

Hence, existence of strong chemical bond in comparison with hydrogen bond between starch and pargasite surface explains decrease of its floatability compared to quartz in process of iron ore flotation and forces to search new conditioning reagent modes.

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